

ON THE DEFINITION OF ASPHALTENES

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INTRODUCTION

Projected shortages of liquid fuels have led refineries to "look deeper into the barrel" for further sources of hydrocarbon liquids. Thus, the heavy ends of petroleum are assuming a "popularity" never before imagined. It is, however, the misfortune of these heavier fractions to be rich in the asphaltene portion of petroleum which is not very amenable to refinery processes and is usually responsible for coke lay-down and catalyst inefficiency. Thus, a considerable effort has been applied to defining asphaltenes in terms of structural and functional moieties on the presumption that knowledge of the structure will assist in the design of suitable conversion sequences in the refinery.

The present definition of asphaltenes is based on the solution properties of petroleum residua, bitumens and the like in various solvents (1,2,3) and there has been considerable scientific effort to further define asphaltenes in terms of molecular structures (4,5,6). Nevertheless, it must always be recognized that asphaltenes (from whatever the source) are, in fact, a solubility class (Figure 1) and that the definition is, in fact, an operational one; that is, asphaltenes are soluble in light aromatics such as benzene or toluene and insoluble in light paraffins such as pentane, hexane, heptane, etc.

In addition, there also has been a growing tendency to classify asphaltenes by the particular paraffin used to precipitate them from the benzene-soluble portion of the feed. Thus, there are pentane-asphaltenes, hexane-asphaltenes, heptane-asphaltenes, and so on with the yield of paraffin-insolubles decreasing with increasing carbon number of the paraffin (9,10,11). For example, whereas liquid propane will precipitate approximately 50% of Athabasca bitumen as "asphaltenes" the yields of asphaltenes using n-pentane, n-heptane and n-decane are 17%, 11% and 9%, respectively (10), with very little difference in the amount precipitated for higher molecular weight n-paraffins (10,11). However, it must be stressed that the addition of a minimum of 40 volumes of the liquid hydrocarbon is required for complete precipitation of the asphaltene fraction; use of much lower proportions of the precipitating medium may lead to errors not only in the determination of the amount of asphaltenes in the crude oil but also in any ensuing determination of compound types in the asphaltene fraction. For example, when insufficient proportions of the precipitating medium are employed, resins are adsorbed onto the asphaltenes from the supernatant liquid and can be released later by reprecipitation (12). Thus, questionable isolation techniques throw serious doubt on any conclusions drawn from any subsequent work with the isolated material.

In short, there are many shortcomings in the methods described for the separation of asphaltenes and the techniques employed for such endeavors are often quite diverse, ill-defined, difficult to interrelate and difficult to apply to the wide variety of complex materials that fall into the classification of petroleum, bitumens and residua (13).

Another aspect of the science that has received some attention is the delineation of the molecular size of the asphaltenes in terms of molecular weight data. Determining the molecular weight of asphaltenes is a problem because they have a low solubility in the liquids often used for determinations and, since asphaltenes tend to associate, even in dilute solution (14,15), there has been considerable conjecture about the actual molecular weights of these materials. For example, ultracentrifuge studies give molecular weights up to 300,000 (14,16,17) while an osmotic pressure method (18) indicated molecular weights of approximately 80,000 and a monomolecular film method (19) yielded values of 80,000 and 140,000. However, other procedures have yielded lower values: 2500 to 4000 by the ebullioscopic method (20); 600 to 6000 by the cryoscopic method (21,22,23,24); 900 to 2000 by viscosity determinations (16,25,26); 1000 to 4000 by light adsorption coefficients (27); 1000 to 5000 by vapor pressure osmometry (28,29); and 2000 to 3000 by an isotonic (30) or equal vapor pressure (31) method. Thus, it is evident that the nature of the asphaltenes is not conducive to the determination of "absolute" molecular weights by any one particular method (15).

A fairly comprehensive study of asphaltene molecular weights by vapor pressure osmometry (32) shows that the molecular weights of various asphaltenes are dependent not only on the nature of the solvent but also on the solution temperatures at which the determinations were performed.

Obviously, all of these observations are of some significance in the formulation of molecular structures of asphaltenes not only in terms of degree but also in terms of the causes of the variation in the range of molecular weights. Thus, those methods which may involve incomplete precipitation of the asphaltenes or which allow the incorporation of resin material into the asphaltene not only lead to errors in estimation of the composition of crude oils but also lead to errors in determining the molecular types which are predominant in the asphaltenes.

It is, therefore, the intention of the present paper to provide a selective review of the methods which have been employed for the determination of asphaltenes in petroleum, heavy oils, bitumens, and residua with special emphasis on the applicability of these methods. In addition, the influence of the method of separation (or purification) on the molecular weight of the asphaltenes is examined in some detail.

EXPERIMENTAL

Asphaltenes were isolated from Athabasca bitumen in the manner described elsewhere (10) and involved reprecipitation of the asphaltenes from benzene (1g: 1 ml.) by n-pentane (40 volumes) or by n-heptane; in addition the asphaltenes received additional "purification" by repetition of the reprecipitation procedure. In a separate experiment, pyridine was used instead of benzene for the first and subsequent reprecipitation procedures. The untreated asphaltenes were also continuously extracted (Soxhlet) for 24 hours (by which time the extracts were colorless) with n-pentane.

RESULTS AND DISCUSSION

Asphaltene Separation

Asphaltenes are dark brown to black friable solids that have no definite melting point and, when heated, usually intumesce, then decompose leaving a carbonaceous residue. They are obtained from petroleum and bitumens by addition of a nonpolar solvent having a surface tension lower than 25 dynes cm^{-1} at 25 degrees Celsius (such as liquefied petroleum gases, the low-boiling petroleum naphthas, petroleum ether, pentane, iso-pentane, hexane, and the like) but are soluble in liquids having a surface tension above 25 dynes cm^{-1} , such as pyridine, carbon disulfide, carbon tetrachloride, and benzene (10,33).

The standards for asphaltene determination have been prescribed in exact detail but there are, obviously, many variations that can be employed without even considering the variations in precipitant (Tables 1 and 2). Thus, although the substitution of n-heptane by n-pentane as the precipitating medium for asphaltenes may, in itself, not appear as a significant change in the method, the respective yields of asphaltenes will differ markedly (10). There have been strong arguments in favor of either precipitant and have varied from the "complete" precipitation of asphaltenes by n-pentane to the precipitation of "pure" asphaltenes by n-heptane. In the latter case, the "purity" of the asphaltenes is considered to be secured by the lower molecular weight asphaltenes (or higher molecular weight resins?) remaining in solution. Obviously, the purity of the precipitant will also affect the yield of asphaltenes as will the precipitant to oil ratio (10).

Other predominant effects which influence the yield (and quality) of the asphaltenes are (a) use of a solvent to solubilize the oil prior to precipitation; (b) the ratio of solvent to precipitant; (c) the ratio of oil to precipitant; and (d) the contact time of the asphaltenes to supernatant liquid. With regard to (a), asphaltenes may be difficult to obtain in terms of exact quantitatively reproducible amounts if the precipitant is applied directly to certain heavy oils and residua, i.e. it is actually employed to leach soluble material from the mass (12). On the other hand, if (in the absence of a solvent) the oil/precipitant ratio is too low (e.g. 1:20) a situation arises in which there is partial solubilization of the asphaltenes (10,12) because of the effects of the soluble oil components and, hence, there is the need for standard methods to recommend ratios of the order of 1:40. The yield of asphaltenes is close to the asymptotic limiting value when the ratio of oil to precipitant is in excess of 1:20 (12) but if a solvent is used the minimum ratio required is 1:40 (i.e. oil: solvent: precipitant = 1:1:40) thereby ensuring efficient asphaltene separation.

Finally, with regard to (d), there is also fragmentary evidence that (for Athabasca bitumen), when the asphaltenes are allowed to remain in contact with the supernatant liquid for periods in excess of 8 hr., adsorption of resin material will occur from the liquid onto the asphaltenes and can be difficult to remove by washing on the filter pad (12). Other effects such as the use of heat to cause coagulation of the asphaltene particles are also recommended (Tables 1 and 2) but caution is advised if the solutions are to be hot-filtered. An increase in temperature can cause a decrease in the solubility of asphaltic material in the hydrocarbon (10) thereby adding "resin" material to the asphaltene precipitate.

Thus, while the acceptance of a general method of asphaltene determination will be difficult, it is the only means by which exact comparisons of published data can be made. This would require the use of high purity solvents as well as recognition of the intricacies of the method. This latter is particularly important at a time when heavy feedstocks are of increasing significance and at a time when most researchers have modified an already existing technique to satisfy differences in feedstock character or even availability of materials.

In summary, the complex nature of the multitude of feedstocks that are currently in use makes the establishment of a standard method of asphaltene determination almost impossible. The current practice is to employ heptane as the precipitant with or without a solvent (e.g. toluene) although pentane is still frequently advocated as the precipitating medium while, surprisingly, in other than isolated reports hexane has not received the same attention as its two immediate neighbors in the homologous series. Obviously, the problem needs to be resolved so that comparisons of published data can be made on a fair basis. In fact, it appears that heptane is receiving increasing acceptance as the precipitant for the determination of asphaltenes in petroleum, heavy oils, bitumens, and residua.

Asphaltene Molecular Weights

There has been considerable discussion on the variation of asphaltene molecular weights (above) and some question as to whether or not the values derived by the various methods are absolute (15). The variations in the data obtained by any one particular method are real (32) but the reasons for this variation have remained speculative. There has also been some speculation about the molecular weight variations induced by the presence of adsorbed or occluded "resin" material*. In fact, the data reported herein (Table 3) affords very strong evidence to support the contention that resin material is occluded within the asphaltene matrix during the precipitation procedure. In each case, the removal of lower molecular weight resin material gives rise to higher molecular weights of the purified asphaltenes. It is, of course, presumed that the use of pentane throughout as the controlling medium did not cause loss (or removal) of any lower molecular weight asphaltenes.

In addition, the use of heptane as the precipitating medium (Table 3) also produced an asphaltene fraction that was contaminated by resin (heptane-soluble) material and which also influenced the molecular weight of the fraction. Again, reprecipitation (three times with heptane) removed this material thereby causing a rise in the observed molecular weights. Finally, the molecular weights of the "purified" asphaltenes also varied with the solvent used for the determination (Table 3) in the manner noted previously (32); i.e. solvents of high dielectric constant decrease the observed molecular weights.

The tendency of asphaltenes to exhibit association/dissociation characteristics depending upon the nature of the solvent is also true for a series of higher molecular weight fractions. However, it should be noted here that although the results with these particular (Athabasca) asphaltenes and with asphaltenes available from other crude oils (32) suggest that molecular weight varies with dielectric constant of the solvent, there may be other factors not yet investigated, which may, in part, also contribute to this phenomenon.

Obviously, the major finding is that resins occluded within the asphaltene during the separation procedure affects the apparent size of the asphaltene "molecules" in various solvent. The concept that asphaltenes release the final vestiges of this resin only upon swelling by a solvent such as pyridine is also worthy of note. If the structural types in petroleum are actually a continuum of the same type from one fraction to another (especially, in this context, from the resins to the asphaltenes) there is little to be inferred from this study other than the influence of degree of association. On the other hand, if the structural types vary from the resins to the asphaltenes, it may be necessary to re-assess the distribution, and even the concepts, of molecular types that have been proposed heretofore.

In summary, it is obvious that asphaltenes are difficult to define even when a standard method of precipitation is employed. The many variations in the recommended procedures (Tables 1 and 2) may all have some influence not only upon the yield but also upon the chemical nature of this complex fraction. Indeed, the molecular weight study reported herein indicates, to some degree, the major variations that can occur in this relatively "simple" molecular parameter. It is, therefore, obvious that asphaltenes are not only a complex chemical fraction but also a complex physical fraction that is extremely difficult to define whether they arise from petroleum (33,34,35) or coal liquids (36).

* Pentane-soluble material and it is presumed that analogous phenomena would be observed for hexane-precipitated or heptane-precipitated asphaltenes.

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Table 1

Analytical Procedures for the Determination of Asphaltenes using Heptane

<u>Test No./Title</u>	<u>Solvent(s)</u>	<u>Sample/Solution Heated</u>	<u>Solvent(s)/gm Sample</u>	<u>Standing Time</u>
IP 143/57 Normal Heptane Insolubles	n-Heptane >99+ mol% (Pure grade)	Slightly/No/ Warm For Filtering	100 ml nC ₇ /gm	1 hour cooling
ASTM D3279-76 Normal Heptane Insolubles (9/24/76)	n-Heptane 99 min mol% (Pure grade)	Slightly/ Reflux	100 ml nC ₇ /gm	1 hour cooling
IP 143/77 Asphaltenes Pre- cipitation with Normal Heptane	n-Heptane, Toluene (or Benzene)	No/Reflux	30 ml nC ₇ /gm	Cool for 1.5-2.5 hr in dark
Proposed Methods for Asphalt Com- position Analysis (ASIM) (May, 1977)	n-Heptane 99+ mol% Pure grade	If needed/ Yes	100 ml nC ₇ /1 ml	Over- night

Table 2

Analytical Procedures for the Determination of Asphaltenes using Pentane

Test No./Title	Solvent(s)	Sample/Solution Heated	Solvent(s)/gm Sample	Standing Time
ASTM D893-69 (Procedure A) Insolubles in Used Lubricating Oils (10/3/69)	n-Pentane Commercial grade	To 65-5°C to suspend all solids, filter through 150 m before adding solvent/room temperature	10 ml nC ₅ /gm	3 hour max.
Syncrude Analytical Method for Asphaltenes in Bitumen	n-Pentane, Commercial; Benzene, ACS reagent	If necessary/ no	1 ml Bz/gm 40 ml nC ₅ /gm	2 hours
ASTM D2006-70 Characteristic Groups in Rubber Extender and Processing Oils by Pre- cipitation Method (2/27/70) (Discontinued)	n-Pentane Commercial	Yes/No	50 ml nC ₅ /gm	15 hours
ASTM D2007-75 Characteristic Groups in Rubber Extender and Processing Oils by the Clay-Gel Adsorption Chromatographic Method (8/29/75)	n-Pentane Commercial	No/Yes	10 ml nC ₅ /gm	30 min.

Table 3

Variation of Molecular Weight of Pentane-Precipitated Asphaltenes

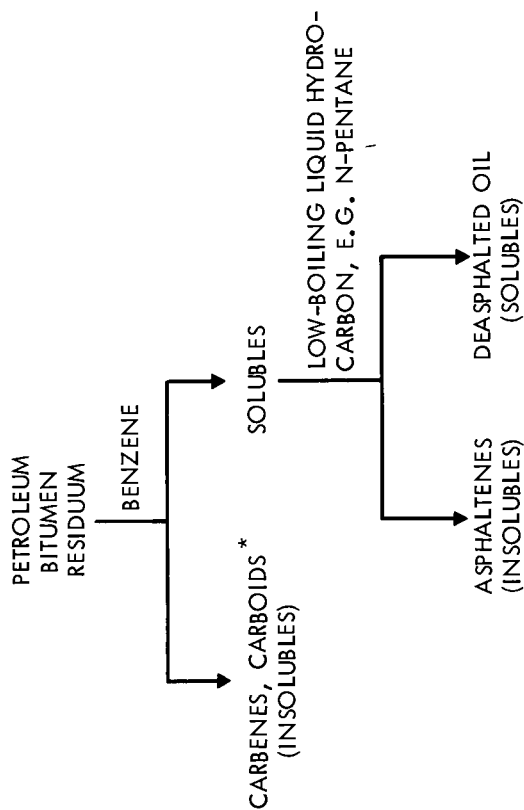
Asphaltenes	wt. %	Solvent*	Molecular Weight			
			C ₆ H ₆	CH ₂ Br ₂	C ₅ H ₅ N	C ₆ H ₅ NO ₂ **
A. Pentane	100		4050	2730	2310	1610
reprecipitated (1)	93		5120	3380	2590	2010
resin	7		710			
reprecipitated (3)	89		8710	5810	--	2640
resin	13		797			
reprecipitated (1)***	87		13390	8800	--	2850
resin	13		940			
pentane extracted	90		8450	6740		2820
resin	10		845			
B. Heptane	100		6850	4320	3580	2670
reprecipitated (x3)	92		8560	6890	4310	2880
resin	8		1050			

* Asphaltene concentration: 2.5 w/w; temperature 37°C

** Extrapolated values from data derived at 100°C, 115°C and 130°C

*** Pyridine used instead of benzene

Figure 1



SCHEMATIC REPRESENTATION OF ASPHALTENE SEPARATION.

* In the case of coal liquids, these "insolubles" are often referred to as "preasphaltenes", "asphalts", etc. based on solubility in solvents such as pyridine, quinoline, etc. (7,8).